



# **Prediction of the Impact Sensitivity of Energetic Molecules Using Symmetry Adapted Perturbation Theory**

**by DeCarlos E. Taylor**

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14. ABSTRACT The intermolecular interaction energies of 1,1-diamino-2,2-dinitroethylene (Fox-7), hexanitrobenzene (HNB), 2,4,6-trinitrotoluene (TNT), 1,3,5-trinitrobenzene (TNB), 2,4,6-trinitroaniline (TNA), 1,3-diamino-2,4,6-trinitrobenzene (DATB), and 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) have been computed using symmetry adapted perturbation theory. Using the experimental unit cells, energies of all symmetry unique dimers within the cells were determined and a simple correlation of the largest dimer interaction energy for each energetic with experimentally measured impact sensitivities was established. It was found that this approach properly predicted the experimental trend when the energetics were grouped into compounds of similar chemistry. Specifically, the method correctly predicts the experimental trend for the nitroaromatics (HNB-TNB-TNT) amongst themselves and the nitroanilines (TNA-DATB-TATB) amongst themselves. Based on these results, symmetry adapted perturbation theory appears to be a useful tool for the determination of impact sensitivities with no regard to experimental data other than the chemical class and orientation of the monomers in the unit cell.					
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## 1. Introduction

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The development, production, and fielding of new energetic materials (EM) is an expensive process requiring a large investment in researcher time and resources. Further, for novel compounds that do not meet the U.S. Army's baseline performance metrics, the disposal of the material requires additional resources; this further increases the overall financial liability to the organization. The general production process relies heavily upon experimentation and, generally, given a series of candidate materials, only a few will be retained for actual fielding. As a result, a longstanding effort in EM research is the identification, *a priori*, of candidates that do not meet performance standards so that valuable resources will not be wasted on their formulation, analysis, and ultimate disposal.

A key metric that weighs heavily into the overall assessment of an energetic is its sensitivity. The Army wishes to field high-performing yet highly-insensitive compounds that will not initiate unexpectedly which, needless to say, has critical ramifications on Soldier safety. There are a variety of tests and types of EM sensitivity, including friction, electrostatic discharge, thermal, explosive shock, and impact. One of the more convenient experimental tests of EM sensitivity is the so-called "drop weight impact test" (*1*). In this test, a small amount of the energetic is placed on a striker plate, an anvil (typically, 2.5 kg, though the mass may vary) is dropped from several heights onto the sample, and any evidence of initiation is noted. The target observable in the drop weight impact test is the " $h_{50}$ " value, which corresponds to the lowest height from which at least 50% of the drops yield a response from the energetic. Generally, the higher the  $h_{50}$  value, the more insensitive the energetic.  $h_{50}$  values can range from 11 cm for the very sensitive hexanitrobenzene (2) compound to 490 cm for the very insensitive 1,3,5-triamino-2,4,6-trinitrobenzene (3) energetic. Unfortunately, the drop-weight impact test, though easy to conduct, is not without issue. For example, the results of the experiments are heavily contingent upon the conditions under which the tests were conducted. Therefore, reproducibility of the results is often problematic. This is exemplified by the reported  $h_{50}$  values for 2,4,6-trinitrotoluene, which range from 100 cm to over 250 cm (*1, 2*).

There has been a large effort to establish a correlation between molecular properties computed quantum mechanically with experimentally determined sensitivities. Previous attempts at theoretical predictions have included examination of quantum mechanical partial atomic charges (4), activation energies (5), bond orders (5), and heats of reaction (6). Much work has focused on intramolecular chemistry, with particular attention on the strength of X-NO<sub>2</sub> bonds (X=C,N), the rupture of which can be the initial detonation trigger (7, 8). In addition to this intramolecular chemical analysis, recent work suggests the importance of *cooperative* effects on the properties of energetic molecular crystals (8). As an example, 1,1-damino-2,2-dinitro ethylene (figure 1), also known as Fox-7, has been the subject of several studies. It has been suggested that the

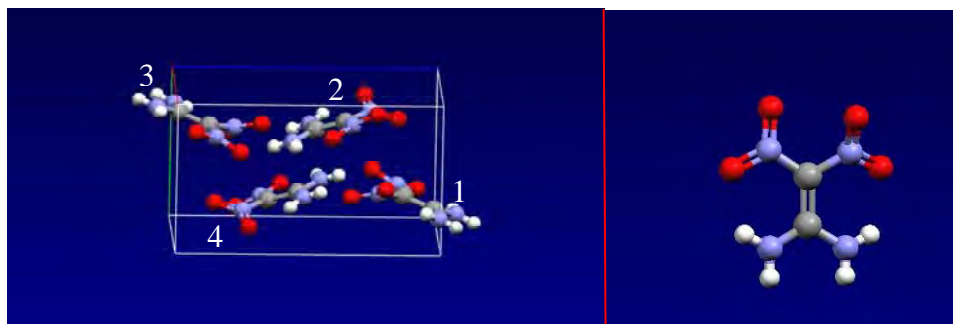


Figure 1. Fox-7 unit cell and single monomer.

formation of an extended intermolecular hydrogen bond network between molecular units leads to the stability of Fox-7 (8–10). Further, Ju et al. (7), using density functional theory (DFT), reported a shortening of C-NO<sub>2</sub> bond lengths in Fox-7 due to intermolecular interactions which, under the assumption that rupture of the C-NO<sub>2</sub> bond initiates detonation, lowers the sensitivity of the energetic since a shorter bond implies more work is necessary for dissociation.

Intermolecular interactions have been studied in a series of explosives; it is well known that they influence a wide array of phenomena such as the crystal packing, diffusion, and defect susceptibility (11, 12). In addition, when mechanical energy is imposed upon a material through impact, the excess energy is dissipated through energy transfer from the low-energy lattice vibrations into the molecular vibrations whose frequencies depend upon the strength of the interaction between constituent molecules. Given the importance of intermolecular interactions on crystal properties, we have conducted a study of the nature of these interactions in a series of energetic crystals using perturbation theory and used this data to draw a direct correlation to experimental impact sensitivities. In this report, we compute the interaction energy of molecular dimers extracted from the unit cells of a series of explosive compounds using perturbative techniques. The dominant physical interaction (electrostatic, dispersion, and induction) between the dimers is identified for each molecular pair, and a simple correlation of the computed binding energy with experimental impact sensitivities is presented, followed by a discussion of future work.

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## 2. Interaction Energies

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Computation of the interaction energy between two molecules using quantum mechanics can be done using the supermolecular approach (13) or, alternatively, perturbative techniques (14). In the supermolecular approach, the interaction energy  $E_{\text{int}}$  of molecules A and B is given by

$$E_{\text{int}} = E_{\text{AB}} - (E_{\text{A}} + E_{\text{B}}) , \quad (1)$$

where  $E_{\text{AB}}$  is the energy of the dimer and  $E_{\text{A}}$  and  $E_{\text{B}}$  are the energies of molecules A and B, respectively. Unfortunately, due to the unavoidable use of a finite basis in quantum chemistry, the supermolecular approach suffers from basis-set superposition error (15). Since the dimer calculation yielding  $E_{\text{AB}}$  necessarily employs a larger basis than that used for each monomer individually, the dimer calculation has more variational flexibility, thus lowering its energy relative to the monomer calculations and resulting in a shift of the computed  $E_{\text{int}}$ . Fortunately, correction schemes such as the counterpoise method (16) can be utilized to remedy the superposition error for interaction energies computed using the supermolecular approach.

As an alternative to the supermolecular approach, the interaction energy within a system can be computed using perturbative techniques where the total interaction energy of the system is written as a sum of terms that arise in increasing orders of perturbation theory (14). Specifically, the total Hamiltonian of the system  $\hat{H}$  can be partitioned as

$$\hat{H} = \hat{H}_{\text{A}} + \hat{H}_{\text{B}} + \hat{V}_{\text{AB}} , \quad (2)$$

where  $\hat{H}_{\text{A}}$  and  $\hat{H}_{\text{B}}$  are the unperturbed Hamiltonians for molecules A and B and  $V_{\text{AB}}$  contains the interaction terms between the two molecules. The target quantity  $E_{\text{int}}$  is simply the expectation value of the dimer wave function with the interaction operator  $V_{\text{AB}}$ . The solution proceeds in a perturbative manner where the energy, evaluated at ever-increasing orders of  $V_{\text{AB}}$ , approaches the exact solution of the full Schrodinger equation. The primary difficulty in intermolecular perturbation theory is enforcing the Pauli exchange symmetry at each order of the perturbation. Specifically, in a perturbative approach, one requires a set of unperturbed functions to be used as an expansion set for the unknown perturbed wave functions. The natural choice for the unperturbed set is a simple product of wave functions from monomers A and B,  $|\Psi_{\text{A}}\Psi_{\text{B}}\rangle$ . However, this simple product is not properly antisymmetric with respect to the interchange of electrons between A and B, violating the Pauli principle. As a result, “symmetry adapted” approaches evaluate the intermolecular interaction using an unperturbed wave function that is properly antisymmetrized at the expense of much more complicated sets of equations (14).

The use of intermolecular symmetry adapted perturbation theories offers advantages over the supermolecular approach. First, perturbative theories do not suffer from the basis set superposition error inherent in the supermolecular approach, and the quality of the computed energy is determined by the perturbative order to which it is evaluated. Secondly, the perturbative approach yields more physical insight into the nature of the interaction than the supermolecular approach. Since the perturbative approach decomposes the total interaction energy into a sum of individual terms evaluated at increasing orders of the perturbation, each term can be associated with a physically meaningful intermolecular force, e.g., electrostatics, dispersion, induction, and this information can be used to specifically characterize the nature of the interaction (13). This level of insight is not possible with the supermolecular approach, which only provides the total interaction energy as a single number.

Computation of the interaction energy of a system requires that the individual wave functions for each monomer be determined, followed by evaluation of the all the terms arising in the intermolecular perturbation series. In terms of computational scaling, this can be a relatively expensive procedure since symmetry-adapted perturbation theory is formally a double perturbation theory, with one perturbation for the intramolecular electron physics and a second perturbation for the intermolecular interactions between the molecules. The intramolecular perturbation can be evaluated using standard methods of quantum chemistry such as many body perturbation theory (17) or coupled cluster theory (17). However, the computational scaling of these methods can be quite steep, limiting the application of the symmetry-adapted perturbation method to small molecules. However, in the late 1990s, Williams and Chabalowski (18) formulated an alternative approach whereby the expensive intramolecular perturbation can be determined using the more economical DFT. This development, known as SAPT(DFT), was not very accurate in its original formulation. However, the idea was expanded upon by Podeszwa et al. (19), and the result is a method that often rivals the most accurate benchmark method available in quantum chemistry, coupled cluster theory for determining interaction energies. In addition to improved accuracy within the SAPT(DFT) model, Podeszwa et al. introduced a resolution of the identity approach (19) (density fitting) that reduced the computational scaling of the original SAPT method from a prohibitive  $N^7$  to a very affordable  $N^5$ , where  $N$  references the size of the computational problem under consideration. This reduction in computational cost renders the SAPT(DFT) method applicable to energetic compounds, which are molecular crystals composed of large monomers that necessitate an efficient quantum chemistry method.

In SAPT(DFT) the total interaction energy (truncated at second order) is given by (19)

$$E_{\text{int}} = E_{\text{elst}} + E_{\text{exch}} + E_{\text{ind}} + E_{\text{exch-ind}} + E_{\text{disp}} + E_{\text{exch-disp}}, \quad (3)$$

where  $E_{\text{elst}}$  describes the electrostatic interactions between the monomers,  $E_{\text{exch}}$  results from antisymmetrization of the wave function as discussed,  $E_{\text{ind}}$  and  $E_{\text{disp}}$  describe the second order induction and dispersion effects, respectively, and  $E_{\text{exch-ind}}$  and  $E_{\text{exch-disp}}$  are modifications to the induction and dispersion energies when exchange effects are accounted for, again via antisymmetrization of the wave function. The survey presented herein is an effort to determine if any correlations exist between the energy components listed in equation 3 with experimentally-determined impact sensitivities for a series of energetic compounds. Specifically, all terms in equation 3 will be evaluated for a series of energetics, and any trends indicative of experimental observations will be established. If such a correlation exists and given the crystal structure of a candidate energetic, the sensitivity of the compound relative to other known energetics can be established using SAPT(DFT) without regard to experiment expediting the formulation of improved, insensitive energetics.

### 3. Computational Approach

Interaction energies for all nonredundant intermolecular pairs in the experimental unit cells for each energetic molecular crystal analyzed in this work were computed using the SAPT2008 suite of programs (20). For a unit cell with  $N$  molecules, there are  $N*(N+1)/2 - N$  unique dimers. However, for symmetric crystals, this number can be reduced as only the symmetry unique interactions need to be evaluated. Each dimer interaction energy was evaluated in a cc-pVDZ basis supplemented by a set of 3s( $\alpha=0.9,0.3,0.1$ ) 3p( $\alpha=0.9,0.3,0.1$ ) 2d( $\alpha=0.6,0.2$ ) 2f( $\alpha=0.6,0.2$ ) midbond functions, where the location of the midbond functions,  $r_{mb}$ , was determined using a weighted average of atom-atom midpoints (21):

$$r_{mb} = \frac{1}{2} \sum_{a \in A} \sum_{b \in B} \omega_{ab} (r_a + r_b) , \quad (4)$$

where the weights  $\omega_{ab}$  are given by

$$\omega_{ab} = \frac{r_{ab}^{-6}}{\sum_{ab} r_{ab}^{-6}} \quad (5)$$

and indices ( $a, b$ ) run over atoms of monomers A and B, respectively. The density-fitting basis required in the SAPT(DFT) approach, consistent with the cc-pVDZ basis used on each monomer, was taken from Weigend et al. (22). The Kohn-Sham orbitals (PBE0 functional) were obtained using a modified version of the DALTON (23) program system, which includes the Fermi-Amaldi asymptotic correction and the splicing scheme of Tozer and Handy (24) with switching values of 3 and 4 (Bragg-Slater radii). The ionization potentials for each compound, required for the asymptotic correction to the Kohn-Sham density, was computed using a delta E calculation for the  $N$  and  $N-1$  electron states of a single monomer extracted from the unit cell. The input ionization potentials used in this work are tabulated in table 1. All calculations were run on 32 cores of an IBM P5 distributed memory computer at the U.S. Navy Defense Shared Resource Center.

Table 1. Ionization potentials of energetic compounds (Hartree).

<b>HNB</b>	0.3144
<b>TNB</b>	0.4516
<b>TNT</b>	0.3408
<b>FOX-7</b>	0.3145
<b>TNA</b>	0.4516
<b>DATB</b>	0.3197
<b>TATB</b>	0.3769

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## 4. Results

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### 4.1 1,1-Diamino-2,2-Dinitroethylene (Fox-7)

Fox-7 contains four monomers in the experimental unit cell (figure 1). This yields six possible dimer interactions. However, only three configurations are unique by symmetry, namely the 1-2, 1-3, and 2-3 dimer pairs, following the monomer labeling indicated in figure 1. Total interaction energies and the corresponding energy components for each configuration are presented in table 2. The largest interaction energy results from the 2-3 interaction, with a value of  $-13.143$  kcal, compared to  $-7.580$  kcal and  $-1.126$  kcal for the 1-2 and 1-3 pairs, respectively. This supports the results of Ju et al. (7), who optimized geometries of Fox-7 dimers using density functional theory and reported the same orientation as the most stable structure. As evidenced by the magnitude of the E(elst) term, the interaction energy for the 2-3 pair is dominated by first-order electrostatic effects. It is well known that exchange interactions are a short-range effect. In terms of their spatial separation, the exchange repulsion term should be most significant in dimer pair 2-3, followed by 1-2, and lastly 1-3, which has the largest center of mass separation of any pair in the cell. This trend is supported by the data in table 2, where the exchange repulsion decreases from 8.047 kcal/mol for the 2-3 pair to 2.712 kcal/mol for the 1-3 pair.

Table 2. SAPT(DFT) interaction energies for the three symmetry unique dimers in the Fox-7 unit cell, following monomer labeling in figure 1 (energies in kcal/mol).

SAPT(DFT) Component	Fox 1-2	Fox 1-3	Fox 2-3
E(elst)	-6.749	-0.220	-13.698
E(exch)	7.521	2.712	8.047
E(ind)	-4.638	-2.009	-4.700
E(disb)	-7.505	-3.011	-4.782
E(exch-ind)	3.062	1.131	1.507
E(exch-disb)	0.729	0.271	0.483
Total energy	-7.580	-1.126	-13.143

### 4.2 Hexanitrobenzene (HNB)

HNB contains four monomers in the experimental unit cell (figure 2). This yields three symmetry-unique interactions. The total interaction energy and components for each dimer extracted from the unit cell are presented in table 3. The largest interaction energy results from the 1-2 interaction and the largest contribution to the total energy for this pair are also due to the first-order exchange repulsion followed by the attractive dispersion interaction. The 1-2 interaction consists of a stacking of monomers, whereas the 2-3 interaction is composed of molecules within the same plane. The out-of-plane stacking dispersion interaction provides 3.2 kcal/mol of additional stabilization compared to the in-plane contribution.

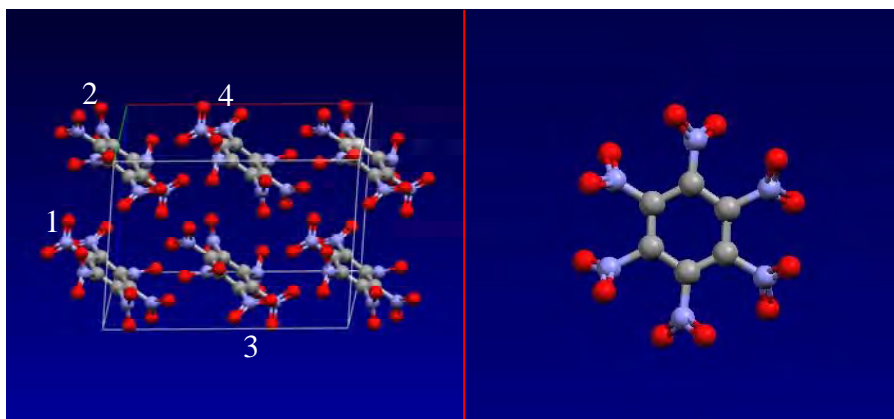


Figure 2. HNB unit cell and single monomer.

Table 3. SAPT(DFT) interaction energies for the three symmetry unique dimers in the HNB unit cell, following monomer labeling in figure 2 (energies in kcal/mol).

SAPT(DFT) Component	HNB 1-2	HNB 2-3	HNB 1-4
E(elst)	-4.142	-1.689	-1.099
E(exch)	8.392	4.482	3.058
E(ind)	-4.285	-2.091	-1.359
E(disg)	-7.548	-4.389	-3.577
E(exch-ind)	3.418	2.073	1.339
E(exch-disg)	0.593	0.355	0.247
Total energy	-3.572	-1.259	-1.391

### 4.3 2,4,6-Trinitrotoluene (TNT)

TNT (orthorhombic) contains eight monomers in the experimental unit cell (figure 3), resulting in 24 dimers. However, the *a* and *c* lattice vectors of TNT have values of 14.91 and 19.68 Å, respectively. Therefore, many of the dimers have a large center of mass separation; as such, their interaction energies are negligibly small and can be neglected. Using a cutoff of 9.84 Å (half the value of the longest lattice vector), interaction energies of all dimers containing a center-of-mass separation less than the cutoff value were extracted from the unit cell and subjected to SAPT(DFT) analysis. Total interaction energies and SAPT(DFT) components for the lowest three interaction energies are shown in table 4. The largest interaction arises from the 1-4 pair and again is dominated by the exchange repulsion energy.

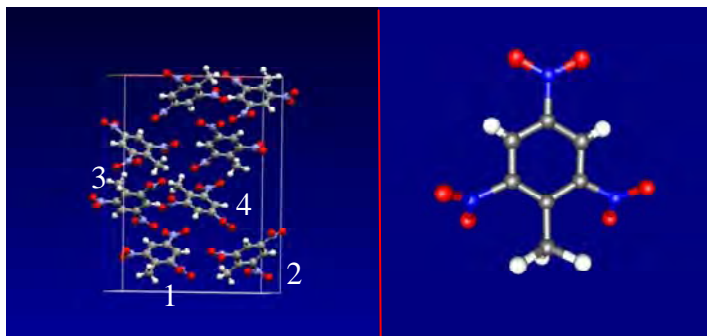


Figure 3. TNT unit cell and single monomer.

Table 4. SAPT(DFT) interaction energies for the lowest energy dimers in the TNT unit cell, following monomer labeling in figure 3 (energies in kcal/mol).

SAPT(DFT) Component	TNT 1-2	TNT 1-3	TNT 1-4
E(elst)	-3.408	-3.710	-6.074
E(exch)	4.745	6.212	7.630
E(ind)	-2.300	-3.119	-4.121
E(dis)	-4.524	-6.382	-6.706
E(exch-ind)	1.834	2.335	3.405
E(exch-dis)	0.416	0.552	0.731
Total energy	-3.237	-4.112	-5.135

#### 4.4 1,3,5-Trinitrobenzene (TNB)

TNB contains 16 monomers in the experimental unit cell (figure 4), yielding 120 dimers. However, the lattice vectors of the orthorhombic unit cell have values of 9.78, 26.94, and 12.82 Å. Therefore, many of the dimers, similar to the TNT cell, have small interaction energies due to the large intermolecular separation. A cutoff of 13.47 Å was used for removal of relevant dimer configurations. Total interaction energies and SAPT(DFT) components for the lowest three interaction energies are shown in table 5. The 1-3 interaction is slightly favorable over the 1-4 pair and, in both cases, the dispersion energy is the dominant contribution to the total interaction energy.



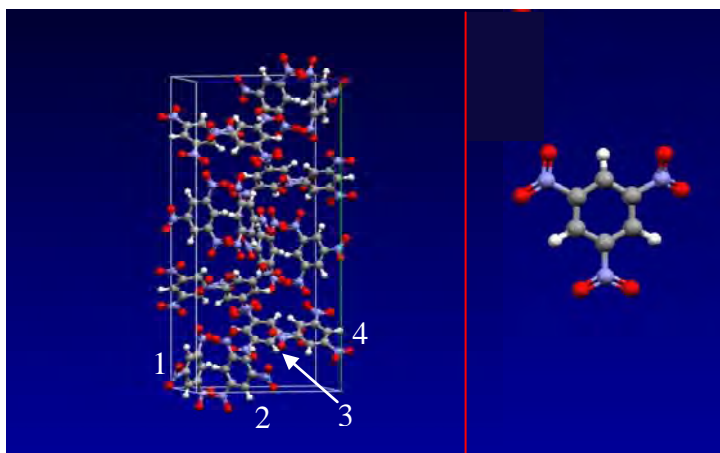


Figure 4. TNB unit cell and single monomer.

Table 5. SAPT(DFT) interaction energies for the lowest energy dimers in the TNB unit cell, following monomer labeling in figure 4 (energies in kcal/mol).

SAPT(DFT) Component	TNB 1-2	TNB 1-3	TNB 3-4
E(elst)	-2.211	-3.784	-2.454
E(exch)	3.993	5.203	4.404
E(ind)	-1.434	-1.839	-1.916
E(disg)	-5.161	-5.279	-5.592
E(exch-ind)	0.801	1.062	1.101
E(exch-disg)	0.287	0.384	0.344
Total energy	-3.725	-4.253	-4.113

#### 4.5 2,4,6-Trinitroaniline (TNA)

TNA contains four monomers in the experimental unit cell, yielding six dimer pairs (figure 5). However, symmetry reduces this to three unique configurations. The largest interaction arises from the 1-3 pair, and, as shown in table 6, the largest component of the interaction energy results from dispersive interactions.

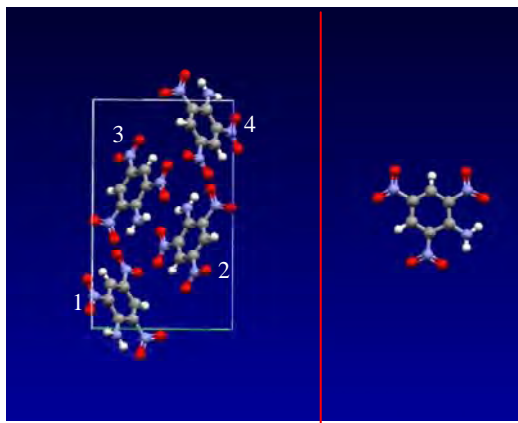


Figure 5. TNA unit cell and single monomer.

Table 6. SAPT(DFT) interaction energies for the symmetry unique dimers in the TNA unit cell, following monomer labeling in figure 5 (energies in kcal/mol).

SAPT(DFT) Component	TNA 1-2	TNA 1-3	TNA 1-4
E(elst)	-2.550	-1.472	-1.921
E(exch)	3.818	5.848	3.042
E(ind)	-1.784	-2.740	-1.099
E(disg)	-4.171	-7.823	-3.621
E(exch-ind)	1.276	2.000	0.793
E(exch-disg)	0.350	0.522	0.263
Total energy	-3.061	-3.665	-2.543

#### 4.6 1,3-Diamino-2,4,6-Trinitrobenzene (DATB) and 1,3,5-Triamino-2,4,6-Trinitrobenzene (TATB)

DATB and TATB each contain two monomers in the experimental unit cell (figure 6), yielding a single dimer pair for SAPT(DFT) analysis. These systems only differ by the addition of one amine group. Similar to TNA, each system has an interaction energy (table 7) dominated by the dispersion interaction, although the TATB dispersive interaction is larger than DATB by more than a factor of 2.

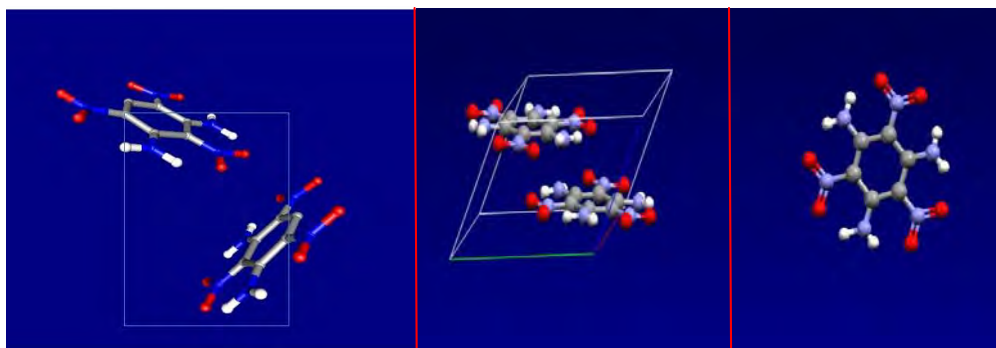


Figure 6. DATB (left panel) and TATB (central panel) unit cell and single TATB monomer.

Table 7. SAPT(DFT) interaction energies for the DATB and TATB unit cells (energies in kcal/mol).

SAPT(DFT) Component	TATB	DATB
E(elst)	-3.924	-3.748
E(exch)	8.589	5.188
E(ind)	-3.465	-2.592
E(disg)	-11.685	-5.393
E(exch-ind)	2.508	1.913
E(exch-disg)	0.773	0.487
Total energy	-7.204	-4.145

## 4.7 Correlation With Experimental Impact Sensitivities

Experimental  $h_{50}$  values (25), for the compounds studied in this work are presented in table 8. A plot of the relative stability normalized to the HNB  $h_{50}$  value via

$$\text{relative stability} = \frac{h_{50}}{h_{50,\text{HNB}}} \quad (6)$$

is shown in figure 7. Represented in this manner, the bars on the plot indicate each crystal's impact stability relative to the HNB baseline, with TATB being the most stable energetic.

Table 8. Experimental  $h_{50}$  values (cm).

<b>HNB</b>	11
<b>TNB</b>	71
<b>TNT</b>	98
<b>FOX-7</b>	126
<b>TNA</b>	141
<b>DATB</b>	320
<b>TATB</b>	490

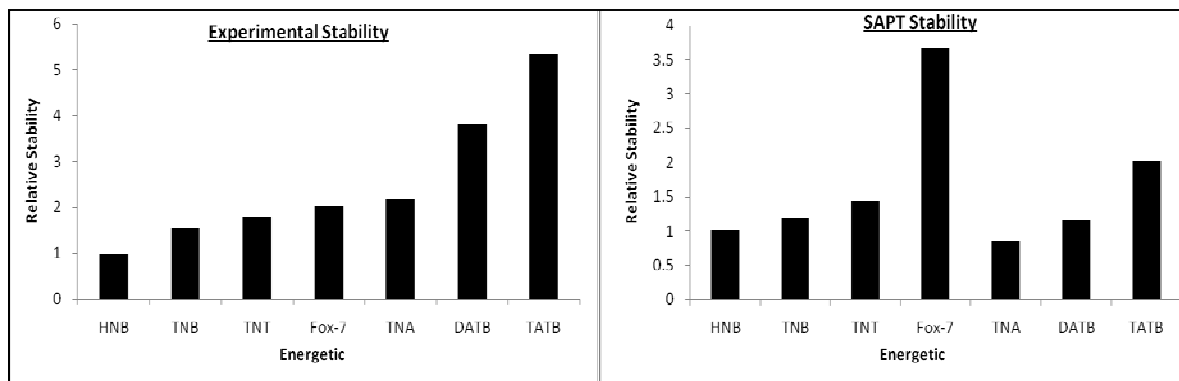


Figure 7. Relative stability of energetic crystals.

The relative SAPT stability for each energetic is determined by dividing the interaction energy of the dimer pair corresponding to the largest interaction energy within each crystal by the SAPT interaction energy computed for HNB, e.g.,

$$\text{relative stability}_{\text{SAPT}} = \frac{E_{\text{SAPT}}}{E_{\text{SAPT,HNB}}} \quad (7)$$

A plot of the relative SAPT stability is also shown in figure 7. It is not expected that the relative SAPT stabilities will quantitatively correspond to the experimental values since the experimental values depend on the conditions of the experiment. For example, if the mass of the anvil used in the experiment is changed, then the  $h_{50}$  values will change as well, possibly shifting their relative magnitudes. However, it is expected that the ordering of the stability predicted by quantum

mechanics will follow the experimental series. The abscissas in figure 7 are ordered by the experimental stability. As a result, the plots should rise monotonically from left to right. Inspection of the SAPT plot shows a proper slope for HNB  $\rightarrow$  TNB  $\rightarrow$  TNT followed by a large increase for Fox-7, breaking the trend. The final three points, however, are properly trending for the TNA  $\rightarrow$  DATB  $\rightarrow$  TATB relative stabilities. Fox-7 is clearly an outlier for the SAPT series. Note, however, that every compound used in this study is a polynitroaromatic, except for the Fox-7 system, which corresponds to nitrosubstituted ethylene. Further, Fox-7 is a difficult system to treat quantum mechanically as the crystal structure is significantly hydrogen-bonded and also has a dependence on weak dispersion interaction occurring between molecular sheets present in the extended structure. Proper treatment of this complicated system requires, at a minimum, a larger basis than the cc-pVDZ basis used in this work and will be the subject of future study.

Focusing on the remaining polynitroaromatic systems, the SAPT plot in figure 7 (neglecting Fox-7) has the proper slope for the first three compounds, drops in going from TNT to TNA, and then rises properly to the end of the series. This break in trend is again attributable to a difference in chemistry. The last three compounds are nitroanilines ( $-\text{NH}_2$  substituents), whereas the first three compounds contain solely  $-\text{NO}_2$  substituted benzene rings. However, if the plots are separated into compounds of similar chemistry, as shown in figure 8, there is indeed a correlation between the quantum mechanically-derived stabilities and experimental trends. The SAPT method yields the same ordering of stability, based on equation 7, as the experimental impact tests; this is a very promising result.

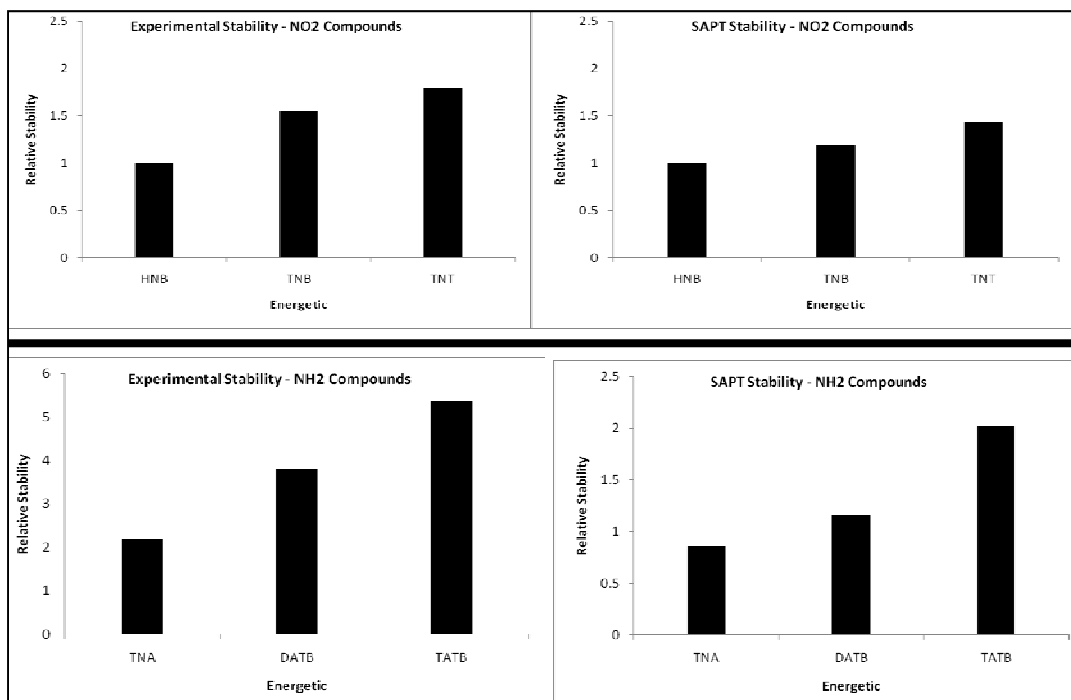


Figure 8. Relative stability of  $-\text{NO}_2$  and  $-\text{NH}_2$  substituted benzene rings.

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## 5. Conclusion

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In this work, we have presented a relatively simple method for predicting the relative impact sensitivity of energetic crystals. With no regard to experiment other than the crystal structure, the relative stabilities have been determined purely from quantum mechanical considerations, although success of the approach requires restriction to compounds of similar chemistry. This situation is not surprising since different chemistries often necessitate different levels of quantum mechanical theory, e.g., higher quality basis sets and/or extended levels of electron correlation, particularly for hydrogen bonded complexes. Further, there may be underlying mechanistic differences between differing classes of compounds that necessitates separate analysis. However, with the caveat that the molecular framework of the analyzed compounds is similar, the method appears to capture the experimental trend for this set of compounds. Future work will involve establishing a trend for a larger data set to identify any limitations of the current approach.

Given the importance of cooperative effects, we are currently computing the energies in a supercell approach where monomers in the central cell interact with monomers in neighboring periodic images. The total energies computed in this way may be indicative of the overall lattice stability, and similar correlations may be drawn to experiment. However, that is a much larger computational effort, and the total data set is still being determined. At present, the current approach appears to show promise. If further analysis utilizing an expanded data set proves successful and given the structure of a candidate energetic, the impact sensitivity can be predicted, a priori, without regard to experimental data using SAPT(DFT), which has been a heretofore difficult task.

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